

PRELIMINARY TEST RESULTS ON A CLOSED-LOOP CONTAMINANT REMOVAL SYSTEM FOR PROCESSING OF METALLIC MELTS

Pramod "K. Sharma, Gregory S. Hickey, and Kin F. Man
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

Abstract

Processing of metallic melts in microgravity containerless experiments requires control of contaminants like oxygen and water vapor to below parts-per-billion (ppb) levels. A significant fraction of contaminants in such materials processing is expected to be generated through outgassing from the heated sample or other parts of the experimental hardware. For space-based experiments, the sample environment control should be achieved with a minimum penalty in system weight and with minimal external streams. A closed-loop system for the removal of trace quantities of oxygen and water vapor which uses replaceable cartridges of zeolite-based sorbents has been designed and fabricated. Systematic tests, exhibiting the feasibility of developing a prototype, have been conducted with a controlled contamination load generated from outgassing of selected metal samples.

INTRODUCTION

Nucleation and undercooling experiments with metallic melts require a very high level of contamination control, particularly for oxygen, water vapor, and solid particulate. Oxygen will lead to an immediate oxide formation with the metallic melt which is a source of heterogeneous nucleation. Similarly, water vapor will form an oxide or hydroxide with several metals. Water vapor also interferes with electrostatic levitation of samples. Solid particulate impurities are also unwanted sources of heterogeneous nucleation.

A closed-loop system for processing of the sample under an inert gas environment has been designed, fabricated and undergone preliminary feasibility tests. This system consists of replaceable adsorbent cartridges for removal of trace oxygen and water vapor; and metallic filters for the removal of solid particulate. The sorbent cartridges are regenerable. The system is designed to be coupled to any microgravity experiment requiring control of above contaminants. The system also has enough capacity to remove oxygen and water vapor contamination generation for a sequence of microgravity ground-based or space experiments. The system exhibits flexibility in temperature range operation and adaptability.

SYSTEM DESCRIPTION

The overall system can be visualized as a contamination control system coupled to an outgassing system with continuous recirculation of an inert gas facilitated by an all metal bellows pump. High purity argon was used as the circulating gas. An AMETEK Model TM-1 B trace oxygen analyzer is also connected in the loop to monitor oxygen levels with time. The overall schematics is shown in Figure 1.

Contamination Removal System

The contamination removal system consists of a bellows pump, a cartridge for oxygen removal and a cartridge for water vapor removal connected in series. In addition, particulate removal is achieved by porous metal filters at the ends of these cartridges.

The bellows pump has a leak rate smaller than 10^{-6} cc/sec. All tubings are of electropolished stainless steel and connected together by VCR fittings. Because the gas comes in contact with only metallic parts, the pump does not add new impurities to the gas. The tubings are welded together so that there are no dead flow zones at the joints or bends. Note that dead flow zones will greatly interfere with the purging of the system.

Oxygen removal to sub ppb range is achieved using a suitable oxygen sorbent packed inside the cartridge. The cartridges can be heated to 300 °C for operation in the scrubbing mode or for regeneration of the spent sorbent. Three classes of novel oxygen sorbents have been developed at JPL, each best suited in its temperature range of operation. These are

- A) Copper exchanged zeolites^{1,2}
(200 -400 °C)
- B) Copper modified carbon molecular sieves^{3,4}
(Room temperature to 250 °C)
- c) Copper or cobalt containing platinum enhanced zeolites⁵
(100 -650 °C)

All three classes of sorbents involve oxygen uptake by catalytic oxidation of the supported metal, i.e. copper or cobalt. The equilibrium level of oxygen removal is well below 1 part-per-trillion (ppt). The details of regeneration (or activation of the sorbent) are described elsewhere.

The cartridge for oxygen removal may be packed with one or a mixture of the oxygen sorbents. Such a design will help in adapting to various design

requirements, e.g. temperature of operation, the initial level of oxygen impurity, duration of the experiments, etc.

Water vapor is removed using pretreated zeolite. This pretreatment consists of drying for 48 hours at 300 °C. The use of such pretreated zeolite for water vapor removal is well known.

Outgassing System

The outgassing system is shown in Figure 2. It consists of a stainless steel chamber which can house a number of metallic strips used as the outgassing sample. The metal strips are packed into the chamber and held in place by a retainer basket. The inside area of the chamber is about 150 cm² while the area of the metal strips can vary from a very low value to about 1000 cm², depending upon the shape and the number of strips used. The outgassing chamber is connected to the rest of the system through VCR fittings.

When the outgassing chamber is heated, outgassing occurs both from the chamber as well as the metal strips. In order to assess the system performance, it is necessary to have the outgassing data from the stainless steel and the metal used in the strips inside the chamber.

In order to interpret the experimental results, data on temperature dependent outgassing is needed for the stainless steel chamber and the metal strips used as a packing inside. These data were obtained separately on an outgassing system designed to measure outgassing rates from metals as a function of temperature. This system consists of a quartz outgassing chamber capable of being heated to 600 °C and connected to a high vacuum system. The chamber is also connected to a mass spectrometer in order to facilitate measurement of the composition of the outgassed species. The cumulative amount of outgassing is determined by recording the pressure inside the chamber as a function of temperature. The outgassing rate is determined from the slope of this curve. Further details on outgassing rate measurement are described in Ref. 6.

The outgassing rates for 316 Stainless Steel and Copper as a function of temperature are shown in Figures 3 and 4, respectively. These figures show overall outgassing. The composition of the outgassed species as a function of temperature is determined separately by mass spectrometric analysis. The relative peak intensities of nitrogen and oxygen can be converted to their mole fractions by a calibration with air.

DEMONSTRATION TEST

The oxygen sorption chamber of the contaminant removal system was packed with 30 g of the reduced oxygen sorbent. This corresponded to a

sufficient capacity to clean up an inert gas flowing continuously at a rate of 100 cc/min and containing 10 ppm oxygen for a period in excess of 200 days. Note that commercial high purity Argon containing 0.5 ppm oxygen is available for purging operations.

The entire system consisting of the contaminant removal subsystem, the bellows pump, and the outgassing chamber were evacuated to 10^{-4} torr level to begin the test from a well defined baseline. A fresh batch of argon gas containing 90 ppm oxygen at a pressure of 5 psig was introduced into the closed loop and recirculated into the system by switching on the bellows pump. The AMETEK oxygen analyzer was turned on and oxygen level was recorded with time for 10 minutes to ensure that there was no air leak into the system from the outside. It is pointed out here that the oxygen level during this interval slowly rose at a rate of about 1 ppm every 3 seconds. This oxygen contamination was attributed to an origin within the oxygen analyzer, probably oxygen adsorbed on the zirconia sensor.

The heating of the oxygen sorption chamber was initiated. When the chamber temperature approached 180 °C, oxygen level began to decrease. With further increase in the chamber temperature, the oxygen level dropped at a faster rate, reaching a level below the sensitivity limit of the instrument of 50 ppb oxygen in about 10 minutes. With the sorbent temperature stabilized around 250 °C, the oxygen analyzer indicated a "zero" reading (i.e., below the sensitivity limit) for oxygen.

Heating of the outgassing chamber was then initiated. The stainless steel outgassing chamber with the packed copper strips was heated from room temperature to 475 °C in a period of 40 minutes and then maintained at this temperature for 30 minutes. The oxygen analyzer reading still stayed at the "zero" level throughout the heating of the chamber. The complete history of variation of the oxygen level with time is shown in Figure 5.

The outgassing data on 316 Stainless Steel and copper obtained as described earlier can be used to obtain total outgassing from combined contributions of the chamber and the packed metal strips. The mass spectrometric data can then be used to compute the oxygen contribution to the total outgassing.

In the test described above, the inside area of the stainless steel chamber was 153 cm² whereas the total area of the packed copper strips was 404 cm². Using the figures 3 and 4, the cumulative outgassing from the chamber surface was 0.68 std. cm³ and from copper strips was 2.50 std. cm³ whereas the combined contributions of copper and the stainless steel was 3.20 std. cm³. Using the mass spectrometric analysis of the outgassed samples and the calibration with air, the oxygen contribution in the outgassed products is about 0.17 std. cm³ from the chamber surface and 0.25 std. cm³ from copper, leading to a total oxygen from outgassing as 0.42 std. cm³. This corresponds to less than 0.3% of the total theoretical capacity for oxygen removal. Hence, it is not

surprising that the oxygen level was maintained at a "zero" reading during the test.

In the second test, the outgassing chamber was initially cold and the closed loop system was run after introducing the Ar-90 ppm oxygen mixture. When the oxygen level had gone down to the "zero" reading and stayed at that level for about 90 minutes, the heating of the oxygen sorbent was stopped and the sorbent chamber was allowed to cool down to room temperature. When the oxygen sorbent was no longer active, the heating of the outgassing chamber was initiated. This caused the oxygen reading to gradually increase due to outgassing from the chamber. As the total outgassing is known from the data in Figures 3 and 4, the oxygen level increase provided a calibration for the oxygen in the outgassed sample.

In a real situation space experiment, oxygen maybe produced at a higher or lower rate than used in this demonstration test. In order to keep the oxygen levels to a low enough level (depending on the experimental requirements), the oxygen removal system may have to be redesigned. However, these tests do show the feasibility of developing a closed loop system for meeting stringent contamination requirements for microgravity experiments conducted in space in inert gas environment.

CONCLUSIONS

The demonstration tests described here show that the concept of a closed loop system **for contamination control of space experiments is feasible**. The design of the closed loop system described here can be improved and made more compact.

ACKNOWLEDGMENTS

The research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA). This work is part of a comprehensive strategy for contamination control/management for NASA's microgravity program. The authors wish to thank Mr. Richard Zanteson for technical help with fabrication of the experimental set up and conducting the tests.

REFERENCES

- 1, Sharma, P. K., and Seshan, P. K., "Activation of Copper Dispersed on a Zeolite for Oxygen Sorption," Chemically Modified Oxide Surfaces, Vol. 3, editors Leyden, D. E., and Collins, W. T., Gordon and Breach, New York, 1990, pp. 65-80.
2. Sharma, P. K., and Hickey, G. S., "A Comparison of the Oxygen Uptake

- Characteristics of Copper Exchanged Zeolite with Copper Dispersed on a Silica Support," Gas Separation & Purification, Vol. 7, No. 3, (1993) pp. 141-146.
3. Sharma, P. K., and Seshan, P. K., "Copper Oxide Modified Carbon Molecular Sieves for Selective Oxygen Removal," Gas Separation and Purification 4, Dec. 1990, p 203.
 4. Sharma, P. K., "Kinetics and Mechanism of Low-Temperature Oxygen Uptake by Copper-Containing Carbon Molecular Sieves," Chemically Modified Surfaces, editors Mottola, H. A., and Steinmetz, J. R., Elsevier, Amsterdam, 1992, pp. 385-394.
 5. Sharma, P. K., "Cobalt based high temperature sorbents for oxygen supported on platinum modified zeolites," NASA New Technology Report, NPO -18409.
 6. Sharma, P. K., and Hickey, G. S., "Thermal outgassing behavior and photoemission studies of Haynes Alloy 214," to be published in the journal Vacuum Science & Technology.

Research
Grade Ar
supply

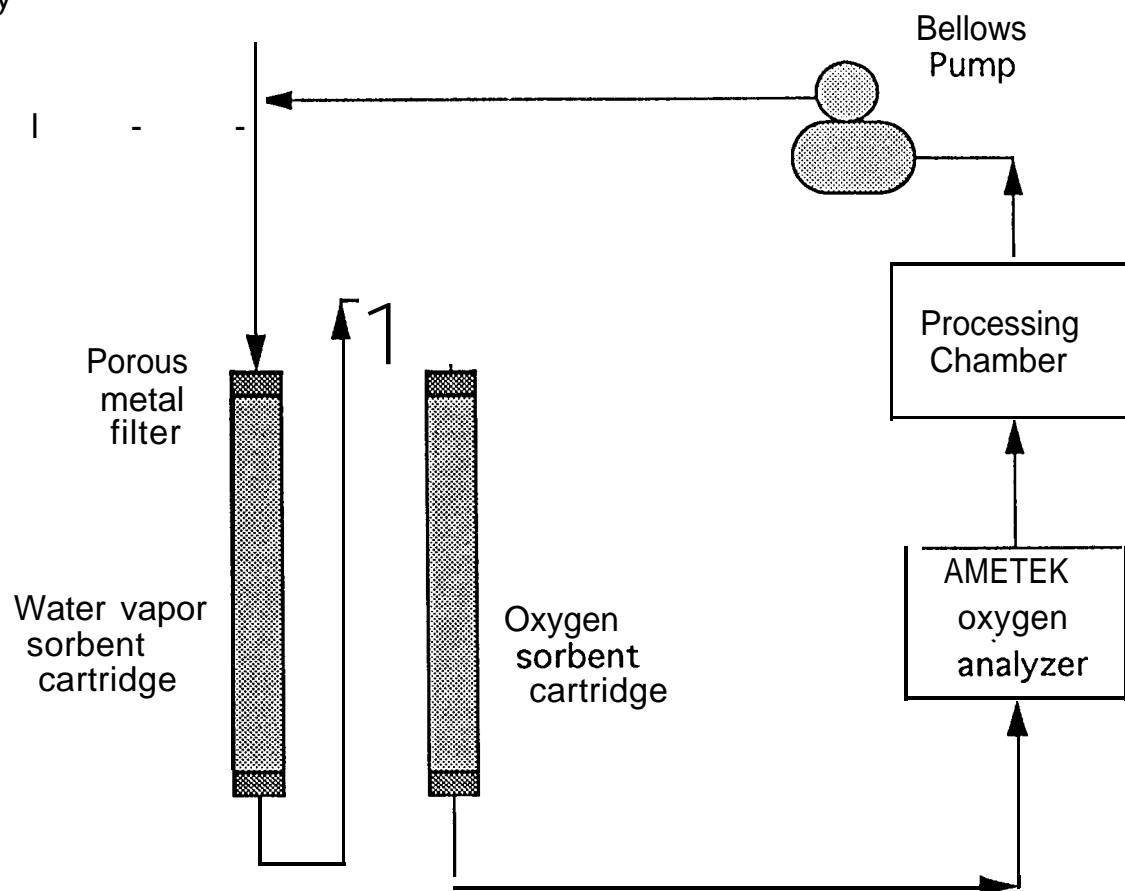


Fig. 1. Schematics of the closed-loop contamination control system

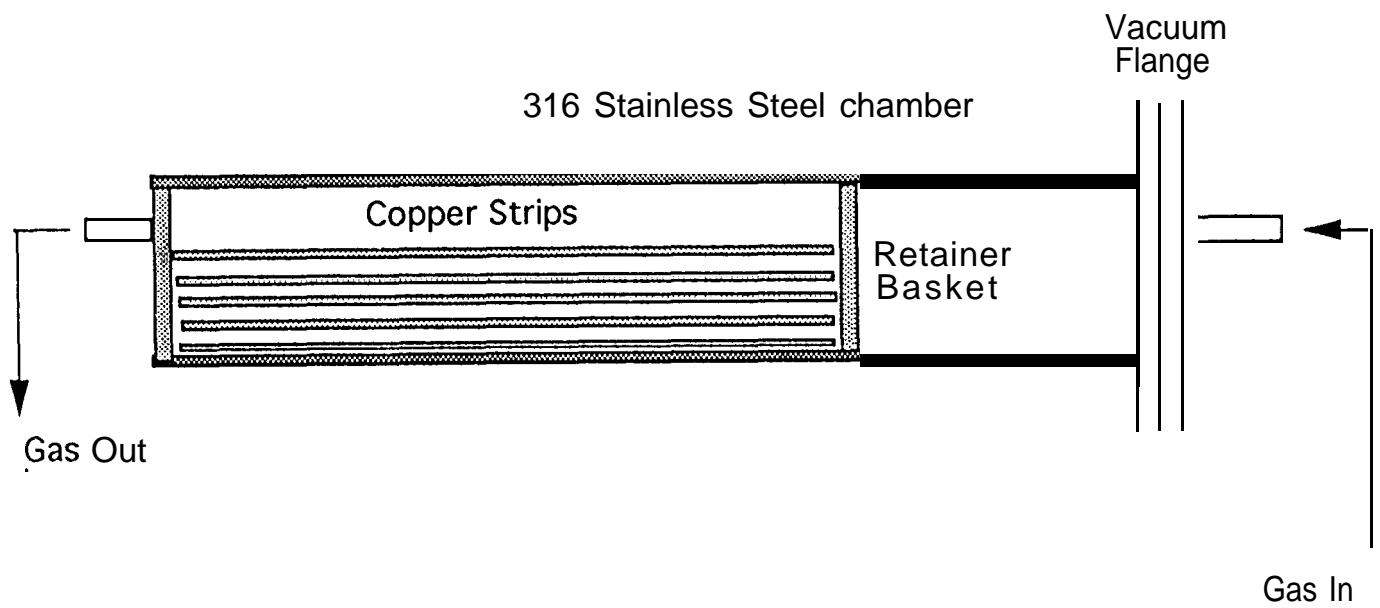


Fig. 2 Outgassing chamber design and layout

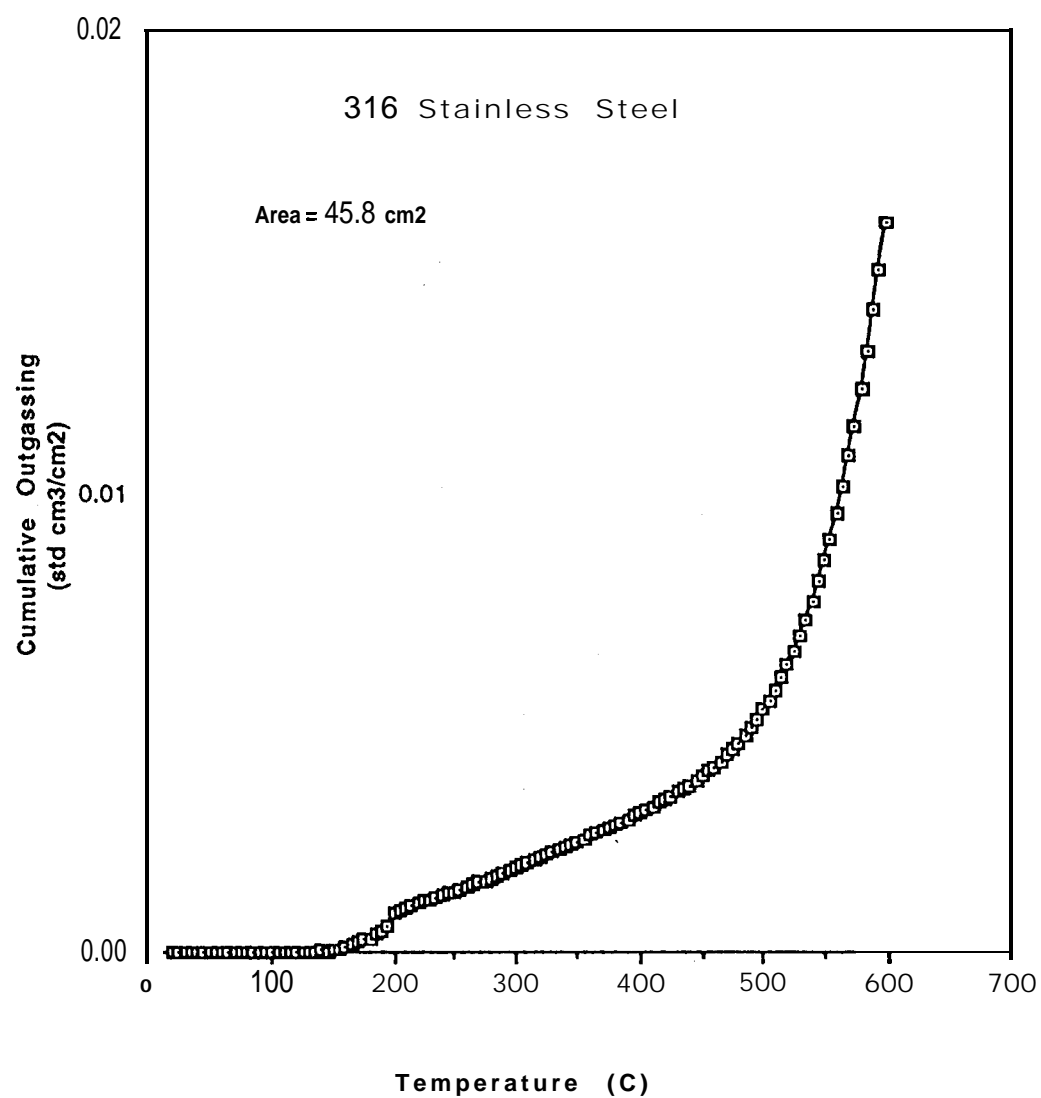


Fig. 3 Cumulative outgassing from 316Stainless Steel asafunction of temperature

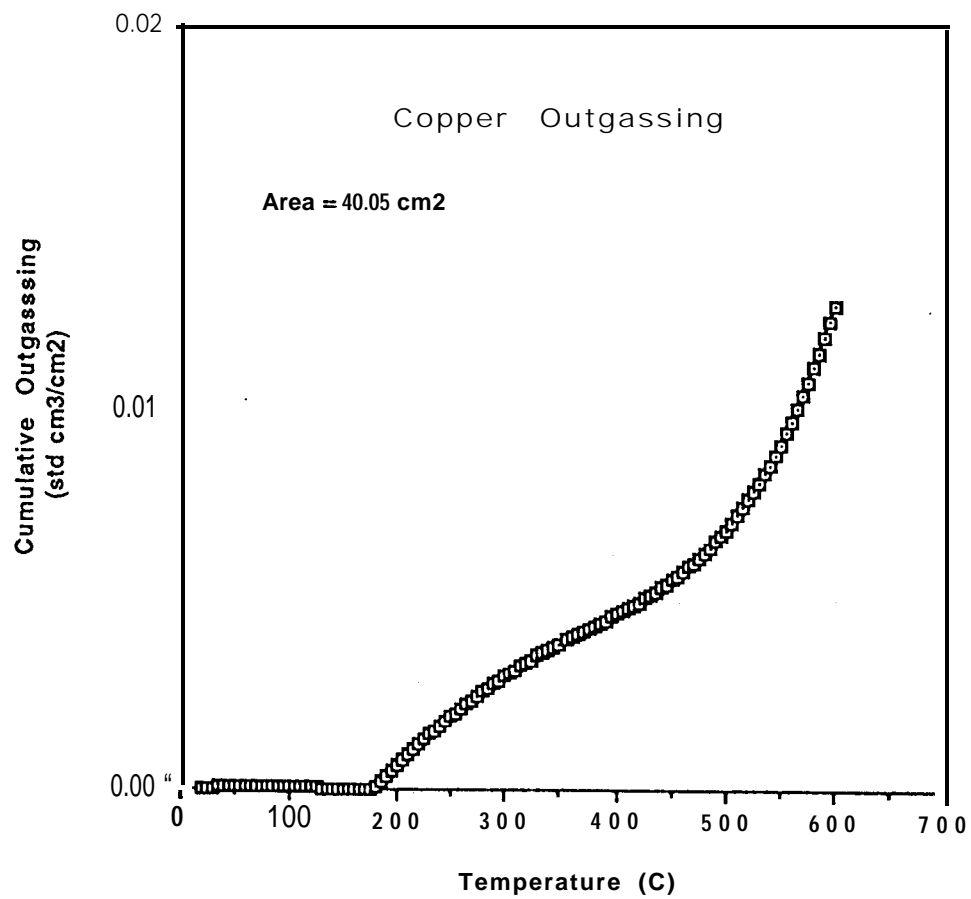


Fig. 4 Cumulative outgassing from copper as a function of temperature

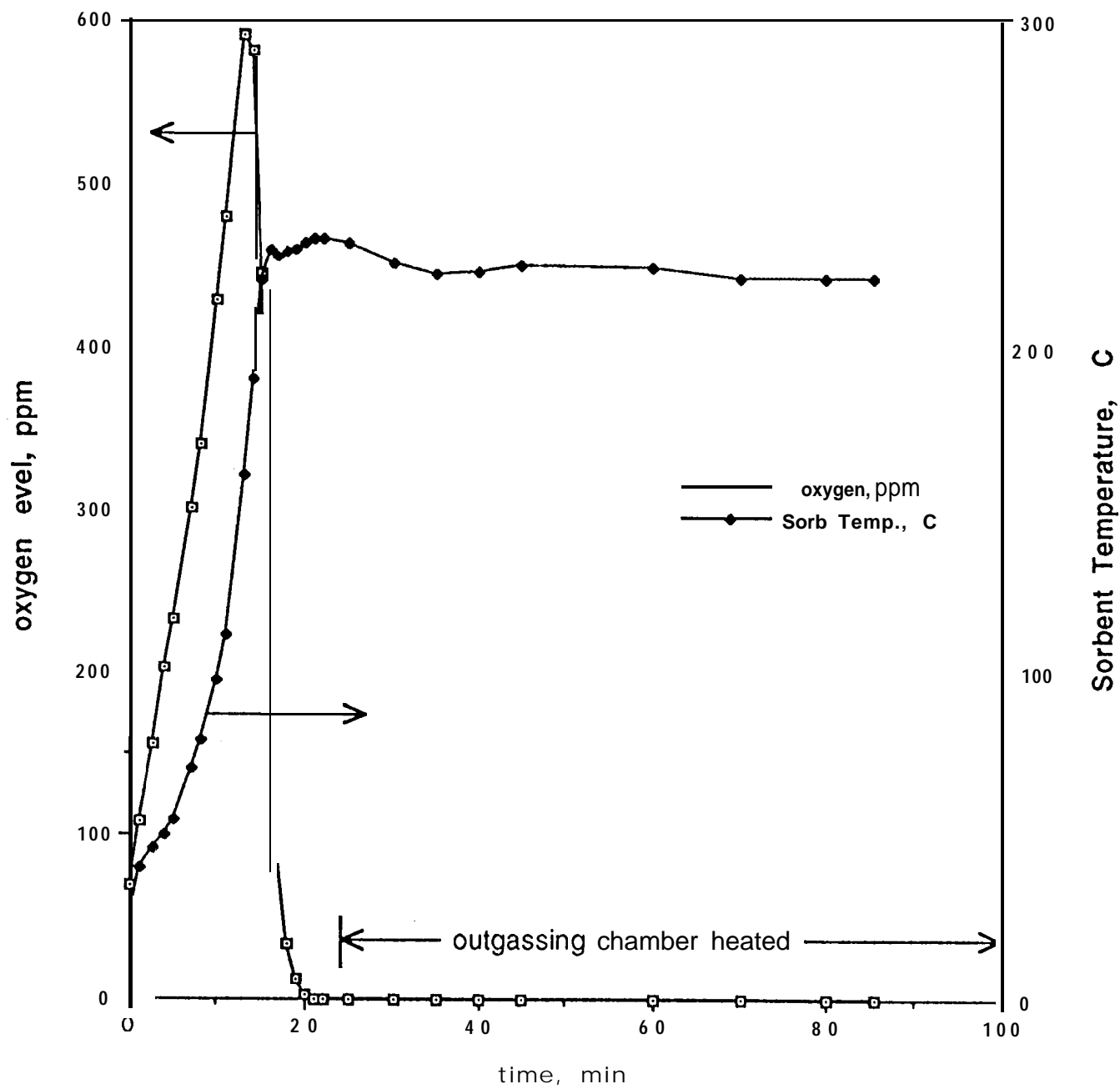


Fig. 5 Graphical representation of the demonstration test